

FORM PTO-1390 (REV 10-96)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER	
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371				Bayer 9930-WCG	
				U.S. APPLICATION NO. (If known, see 37 CFR 1.5) 08/894824	
INTERNATIONAL APPLICATION NO PCT/EP96/00837		INTERNATIONAL FILING DATE 01 March 1996 (01.03.96)		PRIORITY DATE CLAIMED 03 March 1995 (03.03.95)	
TITLE OF INVENTION, POLYSTILOXANE COMPOSITIONS WHICH CROSS-LINK BY CONDENSATION, A PROCESS FOR THEIR PRODUCTION AND THEIR USE, AS WELL AS SURFACE-MODIFIED FILLERS AND THEIR USE					
APPLICANT(S) FOR DO/EO/US Robert Friebe, Wilhelm Weber, and Karl-Heinz Sockel					
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:					
<ol style="list-style-type: none"> 1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. 2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. 3. <input checked="" type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1). 4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date. 5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) <ol style="list-style-type: none"> a. <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau). b. <input checked="" type="checkbox"/> has been transmitted by the International Bureau. c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). 6. <input checked="" type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)). 7. <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) <ol style="list-style-type: none"> a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau). b. <input type="checkbox"/> have been transmitted by the International Bureau. c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input type="checkbox"/> have not been made and will not be made. 8. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). 9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)) and Power of Attorney. 10. <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)). 					
Items 11. to 16. below concern document(s) or information included:					
<ol style="list-style-type: none"> 11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. 12. <input checked="" type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. 13. <input checked="" type="checkbox"/> A FIRST preliminary amendment. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. 14. <input type="checkbox"/> A substitute specification. 15. <input type="checkbox"/> A change of power of attorney and/or address letter. 16. <input checked="" type="checkbox"/> Other items or information: <ol style="list-style-type: none"> a) Copy of published application WO 96/27636 (in German), with copies of the International Search Report, (in German and in English), attached. b) Copy of original Request. c) Copy of International Preliminary Examination Report (in German). 					

U.S. APPLICATION NO (if known, see 37 CFR 1.5)		INTERNATIONAL APPLICATION NO PCT/EP96/00837		ATTORNEY'S DOCKET NUMBER Bayer 9930-WCG	
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17 <input checked="" type="checkbox"/> The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) : Search Report has been prepared by the EPO or JPO \$910.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) \$700.00 No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) \$770.00 Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$1040.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) \$96.00 <div style="text-align: right;">ENTER APPROPRIATE BASIC FEE AMOUNT =</div>				CALCULATIONS PTO USE ONLY 	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	13 - 20 =	0	X \$22.00	\$ 0	
Independent claims	2 - 3 =	0	X \$80.00	\$ 0	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)				+ \$260.00	
TOTAL OF ABOVE CALCULATIONS =				\$ 910.00	
Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28).				\$	
SUBTOTAL =				\$ 910.00	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$	
TOTAL NATIONAL FEE =				\$ 910.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property				\$	
TOTAL FEES ENCLOSED =				\$	
				Amount to be: refunded	\$
				charged	\$ 910.00

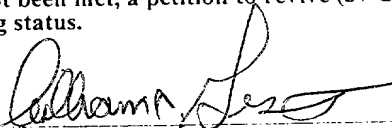
a. ☐ A check in the amount of \$ _____ to cover the above fees is enclosed.

b. ☒ Please charge my Deposit Account No. 02-1445 in the amount of \$ 910.00 to cover the above fees.
 A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any
 overpayment to Deposit Account No. 02-1445. A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO
Mr. William C. Gerstenzang
SPRUNG KRAMER SCHAEFER & BRISCOE
 660 White Plains Road
 Tarrytown, N.Y. 10591


 SIGNATURE:
William C. Gerstenzang

Express Mail mailing label
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27,552
 REGISTRATION NUMBER

Date of Deposit August 29, 1997
 I hereby certify that this paper or fee is
 being deposited with the United States Postal
 Service "Express Mail Post Office to
 Addressee" service under 37 CFR 1.10 on the
 date indicated above and is addressed to the
 Commissioner of Patents and Trademarks,
 Washington, D.C. 20231.

08/894824

Bayer 9930-WCG:cq
Le A 30 576-PUS KK/CS/BS

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s) : Robert Friebe, Wilhelm Weber, and
Karl-Heinz Sockel

Serial No. : To be assigned

Filed : To be assigned

For : POLYSILOXANE COMPOSITIONS WHICH CROSS-LINK
BY CONDENSATION, A PROCESS FOR THEIR
PRODUCTION AND THEIR USE, AS WELL AS
SURFACE-MODIFIED FILLERS AND THEIR USE

Art Unit : To be assigned

Examiner : To be assigned

August 29, 1997

Honorable Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

PRELIMINARY AMENDMENT

In advance of prosecution, kindly amend the above-identified
application as follows and consider the following remarks:

IN THE CLAIMS

Claim 3, line 2, please cancel "one of Claims 1 and 2" and
substitute -- claim 1 -- therefor.

Claim 4, line 2, please cancel "one of Claims 1 to 3" and
substitute -- claim 1 -- therefor.

Claim 5, line 2, please cancel "one of Claims 1 to 4" and substitute -- claim 1 -- therefor.

Claim 6, line 2, please cancel "Claims 1 to 5" and substitute -- claim 1 -- therefor.

Claim 7, line 2, please cancel "Claims 1 to 6" and substitute -- claim 1 -- therefor.

Claim 8, line 2, please cancel "Claims 1 to 7" and substitute -- claim 1 -- therefor.

Claim 9, line 2, please cancel "Claims 1 to 7" and substitute -- claim 1 -- therefor.

Claim 10, line 2, please cancel "Claims 1 to 9" and substitute -- claim 1 -- therefor.

Claim 13, line 2, please cancel "Claims 1 to 9" and substitute -- claim 1 -- therefor.

REMARKS

This Preliminary Amendment is being filed to eliminate multiple dependency.

Favorable action is respectfully solicited.

CONDITIONAL PETITION FOR EXTENSION OF TIME

If any extension of time for this response is required, Applicants request that this be considered a petition therefor. Please charge the required petition fee to Deposit Account No. 02-1445.

ADDITIONAL FEE

Please charge any insufficiency of fees, or credit any excess, to Deposit Account No. 02-1445.

Respectfully submitted,

SPRUNG KRAMER SCHAEFER & BRISCOE

By 

William C. Gerstenzang

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Polysiloxane compositions which cross-link by condensation, a process for
their production and their use, as well as surface-modified fillers and their
use

08/894824

5 The present invention relates to polysiloxane compositions which cross-link by
condensation and contain at least one cross-linkable polysiloxane, at least one
basic filler, at least one phosphorus compound, at least one alkoxy silane cross-
linking agent, at least one organometallic compound and optionally other auxiliary
10 substances, a process for their production and their use, as well as surface-
modified fillers and their use.

15 The polysiloxane compositions according to the invention, referred to hereinafter
as RTV-1 (Room-temperature vulcanizing 1-component) alkoxy systems, are
compositions which are storable with the exclusion of moisture and cure to form
elastomers on exposure to atmospheric moisture with the elimination of alcohols.

20 Products of this kind have been known for a very long time and have been widely
used on the market as sealants. The production of such compositions from OH- or
alkoxy-terminated polysiloxanes, optionally unreactive polysiloxane plasticizers,
alkoxy silane cross-linking agents, catalysts, fillers and optionally other auxiliary
substances is known from US-A 3 294 739, US-A 3 161 614 and
US-A 3 494 951.

25 The material costs of RTV-1 compositions can be considerably reduced by the use
of fillers. The fillers do however not only render the compositions less costly but
they also substantially influence the properties of the RTV-1 alkoxy systems. The
concentration and composition of the fillers used has a crucial effect on the
rheological properties of the unvulcanized compositions, such as their thixotropy
and flow behaviour. They are furthermore important for the mechanical properties
of the cured vulcanizates, such as their tear resistance, elongation at break and
modulus of elasticity. Chalks are for example very frequently used as fillers for
30 RTV-1 compositions. Ground natural chalk is usually used together with
pyrogenic silicic acid. The silicic acid is necessary in this combination if thixo-
tropic compositions are required. Precipitated chalks may be used as an
alternative. These chalks can likewise be combined with silicic acid and also with
natural chalk. However, in sufficient concentrations, they yield thixotropic

compositions even without silicic acid. Sealants which contain precipitated chalk are distinguished by high tear resistance and elongation at break as well as good adhesion and they are therefore very suitable for the typical applications in the RTV-1 field, such as for example as sealants.

- 5 The incorporation of fillers into RTV-1 compositions, in particular at elevated concentrations, can lead to a high increase in viscosity. This high viscosity can cause difficulties in the production of the compositions and also impair their processing. In addition, at high degrees of filling, the modulus of elasticity of the cured sealants increases and their elongation at break is reduced. Precisely the use
10 of precipitated chalks can lead to very high elastic moduli, which are undesirable for the use of the RTV-1 alkoxy systems as sealants. One further disadvantage which can result from the use of the fillers, such as for example the chalks and in particular the precipitated chalks in RTV-1 alkoxy systems, is the reduced storage life of the unvulcanized pastes. If such RTV-1 products are stored with the
15 exclusion of atmospheric moisture and samples are taken from time to time, their cross-linkability suffers as a function of the storage time. Finally they even completely fail to cross-link upon exposure to atmospheric moisture. RTV-1 alkoxy systems generally have shorter storage lives than other RTV-1 compositions. Due to the reduction in their shelf-lives they only have limited
20 applicability.

- The rheological properties of highly-filled RTV-1 polysiloxane compositions can be improved by additives. Different additives have been described in the literature for the various cross-linking systems. Apart from affecting the rheological properties and changing the incorporability of fillers, these additives also change
25 the mechanical properties of the vulcanizates. They usually reduce the modulus of elasticity. By the addition of such auxiliary substances other important properties of the products can however be impaired, such as for example the storage life of the unvulcanized compositions and their adhesive properties.

- 30 Sulphonic acids, and in particular dodecylbenzenesulphonic acid and its salts, are known from EP-A-314 313 and EP-A 314 314 as suitable additives. These sulphonic-acid-containing RTV-1 alkoxy systems result in low moduli of elasticity of the vulcanizates, and the storage life of the unvulcanized products which, without the addition of the sulphonic acid, is relatively small, is not improved by the addition of dodecylbenzenesulphonic acid.

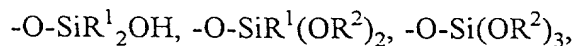
In DE-A-2007002 etherified or esterified polyglycols are used in filled RTV-1 compositions. These products are prepared with the use of various silane cross-linking agents containing at least one nitrogen atom in the molecule, such as for example oximo-, amino- or aminoxysilane cross-linking agents. In DE-A-2 653 499, phosphoric acid esters are described, in combination with the same cross-linking agents. Suitable additives for alkoxy systems that have a low modulus of elasticity and a good storage life are not known.

The problem therefore existed of developing filled RTV-1 alkoxy systems that possess a low modulus of elasticity, high elongation at break and good storage lives in their unvulcanized state. In addition, upon curing they should adhere well to many substrates.

Surprisingly, it has now been found that the known disadvantages of highly-filled polysiloxane compositions that cure at room temperature on exposure to atmospheric moisture and release alcohols as cleavage products can be very largely eliminated if phosphoric acid esters and/or polyphosphoric acid esters are added as additives to the compositions. By means of these additives, both the mechanical properties of the cured rubbers and their storage life in the unvulcanized state are markedly improved.

The present invention provides polysiloxane compositions which cross-link by condensation and contain

- a) at least one cross-linkable polysiloxane that contains as reactive terminal group at least one of the following groups



wherein

- R^1 denotes optionally substituted C_1 - C_8 -alkyl, C_6 - C_{14} -aryl or C_2 - C_8 -alkenyl groups and
- R^2 denotes optionally substituted linear or branched C_1 - C_8 -alkyl or C_2 - C_8 -alkoxyalkyl groups,

and R^1 and R^2 may be the same or different within the molecule,

- b) at least one basic filler and optionally other fillers,
- c) at least one phosphorus compound from the group comprising ortho-phosphoric acid esters of the following formula I



in which

$n = 0, 1$ or 2 and

10 $R^3 =$ an optionally substituted linear or branched C_1 - C_{30} -alkyl, C_1 - C_{30} -acyl, C_2 - C_{30} -alkenyl, C_2 - C_{30} -alkoxyalkyl, C_5 - C_{14} -cycloalkyl or C_6 - C_{10} -aryl group or a triorganosilyl or diorganoalkoxysilyl group which can be the same or different within the molecule,

and/or the esters of polyphosphoric acid,

- d) at least one alkoxysilane cross-linking agent of the formula



wherein

$x = 0$ and 1 , and R^1 and R^2 can be the same or different within the molecule,

- e) at least one organometallic compound and
- 20 f) optionally other auxiliary substances, such as for example plasticizers, bonding agents, stabilizers, pigments, fungicides etc.

Cross-linkable polysiloxanes a) for the purposes of the invention are polydiorgano-siloxanes, preferably polydimethylsiloxanes, wherein the methyl groups may

optionally be partially replaced by vinyl, phenyl, C₂ to C₈ alkyl or haloalkyl groups. The polydimethylsiloxanes are substantially linear, but can contain small proportions of organosiloxy units having a branching effect. In a preferred specific embodiment of the present invention the cross-linkable polysiloxane a) has a viscosity between 0.1 and 1000 Pa.s, preferably between 10 and 500 Pa.s. In addition the cross-linkable polydiorganosiloxane a) can be partially substituted by unreactive groups, such as for example trimethylsiloxy groups.

In a preferred specific embodiment of the present invention the reactive groups of the polysiloxanes are

10 $\text{-O-Si(R}^1\text{)}_2\text{OH}$ groups, in which

$\text{R}^1 =$ an optionally substituted C₁-C₈-alkyl, C₆-C₁₄-aryl or C₂-C₈-alkenyl group, and wherein R¹ may be the same or different within the molecule.

The term substituted includes all the usual substituents, such as for example halogen, NO₂, NH₂, amine, alkoxy, etc.

15 The basic fillers b) are for example precipitated or ground chalk, metal oxides, sulphates, silicates, hydroxides, carbonates and hydrogencarbonates. Other fillers are e.g. reinforcing and non-reinforcing fillers, such as for example pyrogenic or precipitated silicic acid, carbon black or quartz powder. Both the basic fillers and the other reinforcing or non-reinforcing fillers may optionally be surface-modified.

20 Particularly preferred basic fillers b) are precipitated or ground chalks. Component b) can also consist of mixtures of fillers.

The phosphorus compounds c) according to the invention are esters of ortho- and polyphosphoric acid or mixtures thereof. The esters of orthophosphoric acid are described by the following general formula;

25 $\text{O=P(OR}^3\text{)}_{3-n}\text{(OH)}_n$,

wherein

n = 0, 1 or 2 and

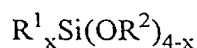
R^3 denotes an optionally substituted linear or branched C_1 - C_{30} -alkyl, C_1 - C_{30} -acyl, C_2 - C_{30} -alkenyl, C_2 - C_{30} -alkoxyalkyl, C_5 - C_{14} -cycloalkyl or C_6 - C_{10} -aryl group or a triorganosilyl or diorganoalkoxysilyl group, and R^3 may be the same or different within the molecule.

- 5 In a preferred specific embodiment of the present invention the phosphorus compound c) is an ester of orthophosphoric acid of the formula I, with at least one optionally substituted linear or branched C_4 - C_{30} -alkyl group R^3 . Where $n=0$ at least one of the substituents R^3 must be triorganosilyl or diorganosilyl radical.

10 Examples of phosphoric acid esters c) according to the invention are primary and secondary esters of orthophosphoric acid as well as mixtures thereof, such as di(2-ethylhexyl) phosphate, dihexadecyl phosphate, diisononyl phosphate, mono-diisodecyl phosphate, mono(2-ethylhexyl) phosphate and tris(trimethylsilyl) phosphate.

- 15 Component c) can likewise be an ester of polyphosphoric acid or a mixture of several polyphosphoric acid esters. Salts of partial ortho- and polyphosphoric acid esters, such as for example alkali metal salts, also are suitable.

Silane cross-linking agents d) in the polysiloxane compositions according to the invention are alkoxysilanes of the general formula



- 20 in which

$x = 0$ and 1 ,

R^1 denotes optionally substituted C_1 - C_8 alkyl, C_6 - C_{14} aryl or C_2 - C_8 alkenyl groups and

- 25 R^2 denotes optionally substituted C_1 - C_8 alkyl, linear or branched C_1 - C_8 alkyl or C_2 - C_8 alkoxyalkyl groups, wherein R^1 and R^2 can be the same or different within the molecule,

or their mixtures.

Preferred alkoxysilanes are tetraethoxysilane, tetra-n-propoxysilane, methyltriethoxysilane, methyltrimethoxysilane, methyltri(2-methoxyethoxy)silane, vinyltrimethoxysilane or vinyltriethoxysilane. Methyl- and vinyltrimethoxysilane are preferred. Component d) can also be a partial hydrolyzate of the alkoxysilane cross-linking agents.

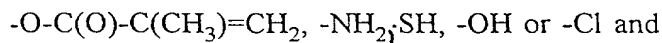
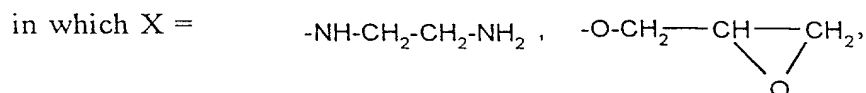
All catalysts which are commonly used according to the prior art in RTV-1 compositions are suitable as organometallic compounds e). Organic titanium and tin compounds are particularly preferred. Cross-linkable polysiloxanes a) containing the reactive groups



are preferably used in combination with organic tin compounds, the groups R^1 and R^2 having the meaning already mentioned. Particularly preferred tin compounds are e.g. diorganotin dicarboxylates, such as dibutyltin dilaurate and dioctyltin maleate as well as solutions of diorganotin oxides in silicic acid esters. Preferred titanium compounds are alkyl titanates, such as for example tetraisopropyl titanate or tetrabutyl titanate and chelated titanium compounds, such as diisobutyl bis(ethyl acetoacetate) titanate, diisopropyl bis(acetylacetonate) titanate or diisopropyl bis(ethylacetoacetate) titanate.

Additives and auxiliary substances f) for the purposes of the invention are preferably plasticizers, bonding agents, pigments and fungicides.

In a preferred specific embodiment of the present invention, the auxiliary substances f) are silicone plasticizers, such as for example polydimethylsiloxanes having terminal trimethylsiloxy groups and a viscosity of 0.1 to 5 Pa.s, bonding agents, such as for example organofunctional silanes of the formulae:



R² has the meaning already mentioned above.

The silicone compositions according to the invention preferably consist of

- 100 parts by weight of a),
- 10 to 250 parts by weight of b),
- 5 0.1 to 25 parts by weight of c),
- 1 to 30 parts by weight of d)
- 0.1 to 20 parts by weight of e) and
- 0 to 240 parts by weight of f).

The total quantity of auxiliary substances and additives f) preferably comprises:

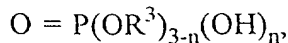
- 10 0-100 parts by weight of plasticizers,
- 0-20 parts by weight of bonding agents,
- 0-100 parts by weight of pigments and
- 0-20 parts by weight of fungicides,

the sum of all the components f) in the mixture being at most 240 parts by weight.

- 15 The present invention also provides a process for the production of the poly-siloxane compositions according to the invention. The components a) to f) are mixed with the exclusion of moisture. Preferably the components a), b) and c) are initially introduced and the other components are then added.

- 20 The phosphorus compounds c) according to the invention are preferably incorporated into the compositions in the course of the production of the poly-siloxane compositions. In a particularly preferred specific embodiment of the present invention the basic fillers b) and the phosphorus compound c), optionally dissolved in a suitable solvent, are mixed in a preliminary operation. Water or polar or non-polar organic solvents, such as for example alcohols and aromatic or
- 25 aliphatic hydrocarbons, can for example be used as suitable solvents.

The present invention also relates to surface-modified fillers which are obtainable by reacting at least one basic filler b) with at least one phosphorus compound c) from the group comprising orthophosphoric acid esters of the following formula I



in which

$$n = 0, 1 \text{ or } 2 \text{ and}$$

5 $R^3 =$ an optionally substituted linear or branched C_1 - C_{30} -alkyl, C_1 - C_{30} -acyl, C_2 - C_{30} -alkenyl, C_2 - C_{30} -alkoxyalkyl, C_5 - C_{14} -cycloalkyl or C_6 - C_{10} -aryl group or a triorganosilyl or diorganoalkoxysilyl group which can be the same or different within the molecule, and/or esters of polyphosphoric acid, if appropriate in a solvent.

10 R³ is preferably C₁-C₃₀-alkyl.

Preferred solvents are water or polar or non-polar solvents, such as for example alcohols, aromatic or aliphatic hydrocarbons and/or polydimethylsiloxanes. These surface-modified fillers are hydrophobic.

15 The present invention also relates to the use of the polysiloxane compositions according to the invention as sealants, adhesives or coating materials.

The present invention also relates to the use of the surface-modified fillers in polysiloxane compositions, plastics, such as for example PVC, thermoplastics, rubber, polysulphide sealants, polyurethane compositions, paints or lacquers.

20 The following examples serve to illustrate the invention without, however, having any limiting effect.

Examples

General procedure for the preparation and evaluation of the compositions

5 The compositions were prepared in a 1-litre planetary mixer in accordance with the examples listed hereinafter. After the preparation the compositions were filled into plastic cartridges and sealed. The material for the appropriate further tests was freshly extruded directly from the cartridges.

10 The cross-linking behaviour of the polysiloxane compositions was tested on a glass plate, for which purpose the pastes were applied in a layer thickness of 2 mm to an area of 40 x 60 mm. After 24 hours the layer of material was cut, peeled off by hand and the underneath surface felt in order to determine whether the layer had cured through to the glass surface.

15 In order to determine the mechanical properties of the vulcanizates, layers of a thickness of 2 mm were produced from the pastes. After leaving the layers to cure for 14 days at 23 °C and 50 % relative atmospheric humidity the vulcanizates were tested according to DIN 53 504. Their hardness was determined after leaving them to cure for 21 days according to DIN 53 505.

20 The storage life of the products was evaluated by storing the pastes in an aluminium tube with a screw cap at 50 °C. Samples were taken at one-weekly intervals and tested for cross-linking. If the samples were perfectly cross-linked 1 week after the extrusion, the test was considered to have been passed. The test for storage life at 50 °C is a method which is commonly used for the evaluation of sealants. It is a quick test for determining the storage life of the products in practice.

Examples 1 to 8

25 In a planetary mixer, 44.0 parts by weight of a polydimethylsiloxane containing terminal $\text{Si}(\text{CH}_3)_2\text{OH}$ groups which had a viscosity of 50 Pa.s at 25 °C were mixed with 45.0 parts by weight of a precipitated chalk (BET specific surface area $19 \text{ m}^2/\text{g}$) which had been treated with stearic acid. Various phosphoric acid esters were added and dispersed in the mixture to form a homogeneous paste. The
30 following compounds were used in the quantities listed in Table 1:

Example 1: di(2-ethylhexyl) phosphate

Example 2: mono(2-ethylhexyl) phosphate

Example 3: monoisodecyl phosphate

Example 4: 1:1 mixture of mono- and di-isononyl phosphate

5 Example 5: trimethylsilyl-di(2-ethylhexyl) phosphate

Example 6: trimethylsilyl-di(2-ethylhexyl) phosphate

Example 7: bis(trimethylsilyl)-mono(2-ethylhexyl) phosphate

Example 8: tris(trimethylsilyl) phosphate

10 Subsequently 8.0 parts by weight of a polydimethylsiloxane containing terminal -O-Si(CH₃)₃ groups and 2.5 parts by weight of methyltrimethoxysilane were stirred in and the composition of the paste was completed by adding 1.0 part by weight of diisobutylbis(ethyl acetoacetate) titanate as well as 0.1 part by weight of N-aminoethyl-3-aminopropyltrimethoxysilane.

15 The compositions of Examples 1 to 8 cured completely within 24 hours. The other properties of the compositions are shown in Table 1.

Comparative Example 9

20 The procedure of Examples 1 to 8 was repeated, the addition of the phosphoric acid ester being omitted. This composition was also completely cured after exposure to moisture for 24 hours. The testing of the storage life and the mechanical properties did however show that the product had inadequate properties. The storage life of only 2 weeks at 50 °C and the poor mechanical properties such as high hardness, low elongation and a high modulus of elasticity, very greatly restrict the possible use of such a product as a sealant.

Comparative Example 10

The procedure of Example 9 was repeated, with the addition of 1.5 parts by weight of dodecylbenzenesulphonic acid. The sealant layer cured completely within 24 hours. The storage life of the product does not differ from that of Comparative Example 5 without any additive and, at only 2 weeks at 50 °C, is inadequate. The mechanical properties of the vulcanizate are of a high standard and include high elongation at break and a low modulus of elasticity (Table 1).

Table 1: Test results of Examples 1 to 10

	Example No.	Parts by weight of phosphate	Shore A hardness	Elongation at break [%]	Modulus of elasticity [N/mm ²]	Tear resistance [N/mm ²]	Storage life ¹⁾ at 50 °C [in weeks]
10	1	1.5	28	880	0.49	2.0	4
	2	1.0	17	820	0.41	1.7	10
15	3	1.1	23	780	0.45	1.7	10
	4	1.3	23	780	0.46	1.8	10
	5	1.0	33	630	0.63	2.0	6
	6	1.25	31	930	0.50	2.34	6
	7	1.0	28	830	0.50	2.11	14
20	8	1.0	30	500	0.45	1.99	14
	9 ²⁾	-	35	640	0.67	2.6	2 ³⁾
	10 ²⁾	1.5 ⁴⁾	24	930	0.44	2.0	2 ³⁾

1) after the indicated time the products were still in a perfect condition

2) comparative example

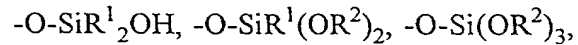
25 3) composition no longer cures after 3 weeks. The product is highly defective.

4) dodecylbenzenesulphonic acid.

Claims

1. Polysiloxane compositions which cross-link by condensation and contain

- a) at least one cross-linkable polysiloxane, that contains as a reactive terminal group at least one of the following groups



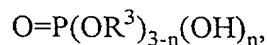
wherein

R^1 denotes optionally substituted C_1 - C_8 -alkyl, C_6 - C_{14} -aryl or C_2 - C_8 -alkenyl groups and

R^2 denotes optionally substituted linear or branched C_1 - C_8 -alkyl or C_2 - C_8 -alkoxyalkyl groups, and R^1 and R^2 can be the same or different within the molecule,

- b) at least one basic filler and optionally other fillers,

- c) at least one phosphorus compound from the group comprising orthophosphoric acid esters of the following formula I



in which

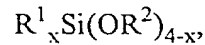
$n = 0, 1 \text{ or } 2$ and

$\text{R}^3 =$ an optionally substituted linear or branched C_1 - C_{30} -alkyl, C_1 - C_{30} -acyl, C_2 - C_{30} -alkenyl, C_2 - C_{30} -alkoxyalkyl, C_5 - C_{14} -cycloalkyl or

C₆-C₁₀-aryl group or a triorganosilyl or diorganoalkoxysilyl group which can be the same or different within the molecule,

and/or an ester of polyphosphoric acid,

- 5 d) at least one alkoxysilane cross-linking agent of the formula



wherein

x = 0 and 1, and

R¹ and R² can be the same or different within the molecule,

- 10 e) at least one organometallic compound and

- f) optionally other auxiliary substances.

2. Polysiloxane compositions which cross-link by condensation, according to Claim 1, characterized in that the cross-linkable polysiloxane a) has a viscosity of between 0.1 and 1000 Pa.s.

- 15 3. Polysiloxane compositions which cross-link by condensation, according to one of Claims 1 and 2, characterized in that the basic fillers b) are precipitated or ground chalks.

4. Polysiloxane compositions which cross-link by condensation, according to one of Claims 1 to 3, characterized in that the phosphorus compound c) is an ester of orthophosphoric acid containing at least one optionally substituted linear or branched C₄-C₃₀-alkyl group R³.
- 20

5. Polysiloxane compositions which cross-link by condensation, according to one of Claims 1 to 4, characterized in that the alkoxysilane cross-linking agent d) is tetraethoxysilane, tetra-n-propoxysilane, methyltri-

ethoxysilane, methyltrimethoxysilane, methyltri(2-methoxyethoxy)silane, vinyltrimethoxysilane or vinyltriethoxysilane.

- 5 6. Polysiloxane compositions which cross-link by condensation, according to Claims 1 to 5, characterized in that the organometallic compound e) is an organic titanium or tin compound.
7. Polysiloxane compositions which cross-link by condensation, according to Claims 1 to 6, characterized in that the auxiliary substances f) are plasticizers, catalysts, bonding agents, pigments and/or fungicides.
- 10 8. Polysiloxane compositions which cross-link by condensation, according to Claims 1 to 7, characterized in that they consist of
 - 100 parts by weight of a),
 - 10 to 250 parts by weight of b),
 - 0.1 to 25 parts by weight of c),
 - 1 to 30 parts by weight of d),
 - 15 0.1 to 20 parts by weight of e) and
 - 0 to 240 parts by weight of f).
9. Polysiloxane compositions which cross-link by condensation, according to Claims 1 to 7, characterized in that the auxiliary substance f) has the following composition:
 - 20 0-100 parts by weight of plasticizers,
 - 0-20 parts by weight of bonding agents,
 - 0-100 parts by weight of pigments,
 - 0-20 parts by weight of fungicides,
- 25 the sum of all the components f) in the mixture amounting to a maximum of 240 parts by weight.
10. Process for the production of the polysiloxane compositions which cross-link by condensation, according to Claims 1 to 9, characterized in that the basic fillers b) and the phosphorus compound c), optionally dissolved in a solvent, are mixed in a preliminary operation.

11. Surface-modified fillers which are obtainable by reacting at least one basic filler b) with at least one phosphorus compound c) from the group comprising orthophosphoric acid esters of the following formula I



in which

n = 0, 1 or 2 and

10 $R^3 =$ an optionally substituted linear or branched C_1 - C_{30} -alkyl, C_1 - C_{30} -acyl, C_2 - C_{30} -alkenyl, C_2 - C_{30} -alkoxyalkyl, C_5 - C_{14} -cycloalkyl or C_6 - C_{10} -aryl group or a triorganosilyl or diorganoalkoxysilyl group which can be the same or different within the molecule, wherein R^3 is preferably C_1 - C_{30} -alkyl, and/or esters of polyphosphoric acid, 15 if appropriate in a solvent.

12. Use of the surface-modified fillers according to claim 11, in polysiloxane compositions, plastics, paints or lacquers.

13. Use of the polysiloxane compositions which cross-link by condensation according to Claims 1 to 9, as sealants, adhesives or coating 20 compositions.

Polysiloxane compositions which cross-link by condensation, a process for their production and their use, as well as surface-modified fillers and their use

Abstract

The present invention relates to polysiloxane compositions which cross-link by condensation and contain at least one cross-linkable polysiloxane, at least one basic filler, at least one phosphorus compound, at least one alkoxy silane cross-linking agent, at least one organometallic compound and optionally other auxiliary substances, a process for their production and their use, as well as surface-modified fillers and their use.

COMBINED DECLARATION AND POWER OF ATTORNEY

ATTORNEY DOCKET NO

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

"CONDENSATION CROSS-LINKING POLYSILOXANE MASSES, A PROCESS FOR PREPARING THE SAME AND SURFACE-MODIFIED FILLERS"

the specification of which is attached hereto,

or was filed on **March 01, 1996**

as a PCT Application Serial No. **PCT /EP96/00837**

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims.

I acknowledge the duty to disclose to the Office all Information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s), the priority(ies) of which is/are to be claimed:

195 07 416.5
(Number)

Germany
(Country)

March 03, 1995
(Month/Day/Year Filed)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)

(Filing Date)

(Status)

(patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status)

(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Le A 30 576-PUS

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